



Kinetic study of the 4-Nitrophenol photooxidation and photoreduction reactions using CdS

Agileo Hernández-Gordillo*, Angela G. Romero, Francisco Tzompantzi, Ricardo Gómez

Universidad Autónoma Metropolitana-Iztapalapa, Depto. de Química, Área de Catálisis, Grupo ECOCATAL, Av. San Rafael Atlixo No. 189, México 09340, DF, Mexico

ARTICLE INFO

Article history:

Received 6 March 2013

Received in revised form 8 July 2013

Accepted 12 July 2013

Available online 2 August 2013

Keywords:

CdS photocatalyst

4-Nitrophenol

Photooxidation

Photoreduction

Na₂SO₃ concentrations

ABSTRACT

We have investigated the kinetics of the photooxidation or photoreduction of 4-Nitrophenol (4-NP) with CdS as photocatalyst, and UV or visible light irradiation in the presence of Na₂SO₃. The photocatalytic reaction was performed by varying the Na₂SO₃ concentration under aerobic or anaerobic conditions, photocatalyst load and 4-Nitrophenol concentration. The 4-NP oxidation was attributed to the formation of the hydroxyl radical at 4 mM Na₂SO₃ concentration in either aerobic or anaerobic conditions under UV light irradiation. The 4-NP reduction was related to the sulfite radicals formed with appropriate Na₂SO₃ concentration (8 mM) in anaerobic conditions under UV or visible light. The 4-NP oxidation and reduction reactions follow a zero order kinetic and can be used as a model reaction to evaluate the active photocatalyst under UV or visible light.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The nitroaromatic compounds are among the most common contaminants present in industrial and agricultural wastewaters that provoke important damages to the environment. Several processes have been proposed for their removal such as adsorption, electro-Fenton, photocatalytic degradation and so on [1–4]. Among the nitroaromatic compounds, the 4-Nitrophenol (4-NP) is probably the most frequent pollutant; 4-NP possesses good chemical and biological stability against natural degradation processes. Several works had studied the photocatalytic degradation of 4-NP in aqueous solution using TiO₂ or ZnO oxides semiconductors as photocatalysts [5–9]. In contrast, the 4-NP can be eliminated by catalytic reduction by metallic nanoparticles (Au or Ag) deposited on different supports such as chitosan-coated Fe₃O₄, SBA-15, Halloysite nanotubes or ZnO [10–14], in the presence of the sodium borohydride (NaBH₄), forming 4-aminophenol (4-AP), which is considered as an important intermediate in the pharmaceutical industries for the manufacture of analgesic and antipyretic drugs, such as paracetamol, phenacetin, acetanilide and so on [15]. In addition, the 4-NP reduction by photocatalytic processes has been achieved with resin-supported dye under visible light [16] and alternatively, our group have reported the photocatalytic reduction

of 4-NP with CdS in the presence of sodium sulfite (Na₂SO₃) under visible light [17].

From these results, it is clear that the photooxidation or photoreduction of 4-NP can be carried out by the use of adequate semiconductors and appropriate concentrations of Na₂SO₃. In this way in the present work we report the kinetic study of the degradation of 4-NP or reduction of 4-NP as a function of Na₂SO₃ concentration. In these photocatalytic reactions, the influence of Na₂SO₃ content in either aerobic or anaerobic conditions, as well as the CdS load and 4-NP concentration was investigated using either UV or visible light irradiation. The structural and optical properties of CdS photocatalyst were characterized by XRD and DRS–UV–vis spectroscopies.

2. Experimental

2.1. Synthesis of CdS photocatalyst

The CdS photocatalyst was synthesized by the precipitation method in an ethylenediamine–water solution at moderate temperature. In a typical procedure, appropriate amounts of Cd(NO₃)₂·H₂O (Reasol) and thiourea (stoichiometry molar ratio 1:2), were dissolved in ethylenediamine–water solutions with 10 vol.% of H₂O at room temperature. The solution was then heated at 110 °C under vigorous magnetic stirring during 24 h. The solid formed was recovered by filtration, washed several times with distilled water and ethanol, and dried at 120 °C for 5 h.

* Corresponding author. Tel.: +52 55 58044668.

E-mail address: agileo12@hotmail.com (A. Hernández-Gordillo).

2.2. Characterization of CdS photocatalyst

The CdS photocatalyst was characterized by X-ray powder diffraction using an X-ray diffractometer Siemens D500 with Cu K α radiation (50 kV, 40 mA). The scanning rate was 0.03°/S in the 2 θ range from 5° to 70°. The band-gap energy was calculated using the Kubelka–Munk method from the diffuse reflectance spectra obtained with a Varian Cary-100 spectrometer equipped with an integration sphere.

2.3. Photocatalytic 4-NP degradation or reduction reaction

The photocatalytic reaction was carried out in a glass home-made reactor system containing 200 ml of an aqueous solution with 10–20 ppm of 4-NP (Aldrich). The amount of Na₂SO₃ (Reasol) was varied from 10 to 400 mg (0.4 to 16 mM) and the mass of the photocatalysts powder ranged from 5 to 50 mg (0.025–0.25 mg/L). The suspension was maintained by magnetic stirring (600 rpm) at room temperature and was left under dark conditions for 30 min. to ensure the adsorption–desorption equilibrium. Subsequently, the mixture was irradiated with either UV light produced by a high pressure Hg Lamp ($\lambda = 254$ nm, $I_0 = 2.2$ mW/cm²), encapsulate into a quartz tube immersed into the solution, or visible light supplied by an LED Lamp (3W) emitting $\lambda = 450$ nm of low luminous fluxes (190 Lumens), located at ~7 cm from the suspension. During the adsorption and photocatalytic reaction process, the suspensions were maintained in either aerobic or anaerobic conditions by bubbling air (O₂ atmosphere) or N₂ gas (N₂ atmosphere), respectively. Similar anaerobic conditions were reached in the absence of bubbled air (without O₂ atmosphere). In all cases, the amount of dissolved oxygen into the suspension was measurement by using Hanna Oxy-Check apparatus to ensure high or low O₂ concentrations. After that the photocatalytic reaction of 4-NP was carried out with different Na₂SO₃ concentrations. The addition of BaCl₂ into the final irradiated suspension was used to confirm the presence of either sulfite (SO₃²⁻) or sulfate ions (SO₄²⁻) by the precipitation of either BaSO₃ or BaSO₄ in acidic (adjusted with HCl) or alkaline media, respectively.

The estimation of the concentration of photoreduced 4-NP was made by UV–vis spectroscopy using a Varian-Cary 100 spectrometer, by following the disappearance of the absorption band at either 345 nm in acid media or 400 nm in alkaline media. The kinetic data such as the apparent rate constant (K_{app}) in both degradation and reduction reactions were obtained considering a pseudo zero order. The Langmuir–Hinshelwood kinetic model is usually applicable to describe the kinetics of 4-NP degradation or reduction on photocatalyst like CdS [12,17]. The disappearance rate (r) and the reactant concentration (C) are related to time (t):

$$r = -\frac{dC}{dt} = \frac{k_r k_{ads} C}{1 + k_{ads} C}$$

where k_r is the rate constant and K_{ads} is the adsorption equilibrium constant.

The plot of (C/C_0) versus reaction time (t) yields a straight line, where the slope is the pseudo zero order apparent rate constant.

3. Results

3.1. Characterization of CdS

3.1.1. X-ray diffraction

Fig. 1 shows the X-ray diffraction patterns for the CdS photocatalyst. The reflection peaks corresponding to the (100), (002) and (101) planes were indexed to the hexagonal phase with lattice parameter close to values previously reported (JCPDS No. 41-1049) for CdS [18]. The relatively strong intensity of the (002) reflection

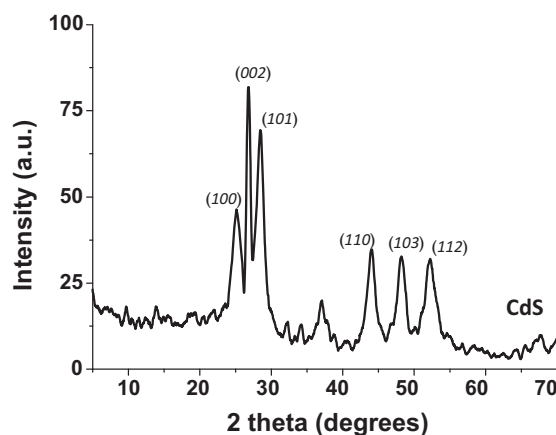


Fig. 1. X-ray diffraction patterns for the CdS photocatalyst.

peak for CdS is indicative of the preferential growth along the c -axis of the hexagonal CdS structure. The average crystallite size for the photocatalyst, determined by the Debye–Scherrer equation from the (002) and (100) reflection peaks, was 16 nm.

3.1.2. UV–vis spectroscopy

Fig. 2 shows the UV–vis diffuse reflectance spectra for the CdS photocatalyst. The photocatalyst exhibits an absorption edge in the visible light region close to 490–520 nm attributed to the intrinsic band-gap transition of an electron from the valence to the conduction band [19,20]. The band-gap energy value of 2.46 eV was estimated by the Kubelka–Munk (K–M) method, extrapolating the linear portion of the $(FR \times hv)^2$ vs hv curves to $FR = 0$ (inserted in Fig. 2). These results would suggest that CdS can be activated with either UV or blue light irradiation. In this case, the shaded area in the Fig. 2 correspond to the emission spectrum of the blue LED lamp used for their activation.

3.2. Oxygen consumption by sulfite ions

Fig. 3A shows the oxygen concentration in the suspension as a function of Na₂SO₃ concentration under dark conditions (adsorption–desorption equilibrium) and in the absence of bubbled air (without O₂ atmosphere). Initially, the O₂ concentration was high (90%), but it decreased as the Na₂SO₃ concentration increased, thus suggesting that the O₂ was consumed by the oxidation of SO₃²⁻ ions [21]. Conversely, rapid O₂ consumption was detected during the first 5 min. of irradiation (photocatalytic reaction

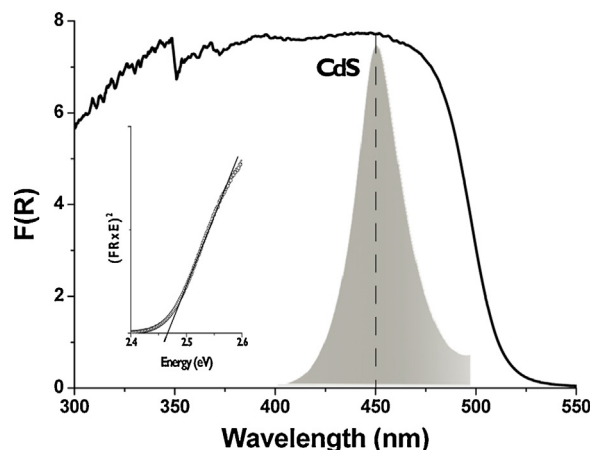


Fig. 2. UV–vis diffuse reflectance spectra for the CdS with K–M plot inside.

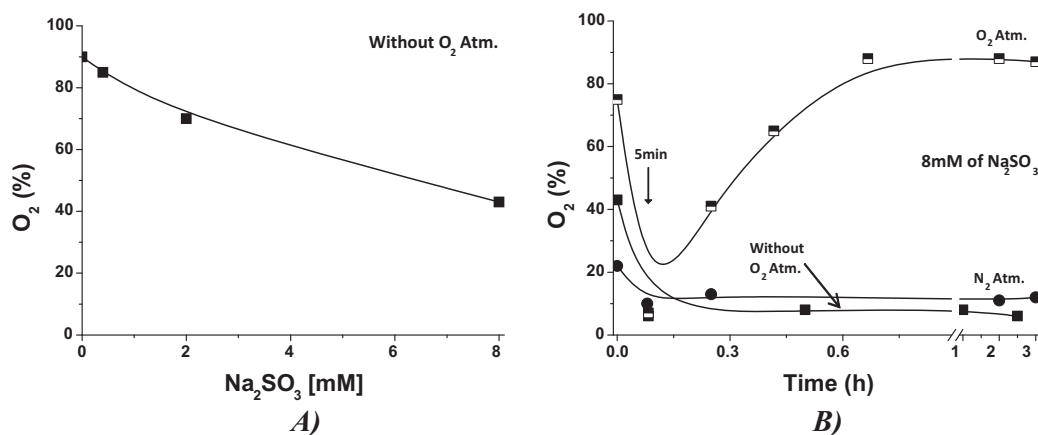


Fig. 3. O₂ profile concentration in the suspensions: (A) as a function of Na₂SO₃ concentrations in absence of bubbled air and (B) as a function of reaction time with 8 mM of Na₂SO₃ in either aerobic or anaerobic conditions.

process), at a fixed concentration of Na₂SO₃ (8 mM) in anaerobic conditions, without O₂ atmosphere or with N₂ atmosphere (Fig. 3B). The partial oxidation of the sulfite ions induced an anaerobic condition while the suspension was irradiated, due to the low concentration of O₂ (10%) [21]. In contrast, an aerobic condition was obtained after the total oxidation of the sulfite ions, since the O₂ concentration increased as the time progressed until reaching high concentrations at 45 min. The O₂ atmosphere was achieved (Fig. 3B), since the concentration of dissolved oxygen remained constant during the time of the photocatalytic reaction. The reduction of O₂ may produce HO₂ and H₂O₂ (or OH⁻), whereas the aerobic oxidation of sulfite may produce SO₃⁻, S₂O₆⁻, SO₅⁻ and SO₄²⁻ ions. According to the literature, the sulfite oxidation proceeds by a free radical chain reaction, which may be initiated by any process that effects either the univalent oxidation of sulfite or the univalent reduction of oxygen with the concomitant formation of sulfate (SO₄²⁻) [22].

3.3. UV-vis absorbance for the 4-NP degradation or reduction reaction

The evaluation of the CdS photocatalyst in the photocatalytic reactions shows that the 4-NP photooxidation or the 4-NPhenolate photoreduction reactions can be carried out depending on the Na₂SO₃ concentrations in both anaerobic conditions. In the absence of this reactant or in the presence of an aerobic condition, the degradation process is favored. Fig. 4 shows the UV-vis absorbance

spectra for the 4-NP degradation reaction in the presence of 16 mM of Na₂SO₃ under O₂ atmosphere and UV light irradiation. In this case, when the 4-NP solution (15 ppm) contained 16 mM of Na₂SO₃ two absorption bands at 210 nm and 400 nm could be seen. These bands correspond to the sulfite ions (SO₃²⁻) and to the 4-NPhenolate ion formation, respectively, due to the alkaline conditions generated by the presence of sulfite ions [17]. During the photocatalytic reaction, the absorption band of the SO₃²⁻ ions decreases as the time progresses, suggesting that it is being oxidized to sulfate. The consumption of sulfite ions may cause the modification of the pH to lower values of the irradiated solution and as a consequence it may cause the appearance of the absorption band at 315 nm (dash line in Fig. 4), associated to the 4-NP formation [11,17], thus establishing an equilibrium between the 4-NP and 4-NPhenolate species. However, the disappearance of the absorption band at 345 nm (isosbestic point, I.P.) as the time progressed, indicates that both species were eliminated through a degradation process. In addition, the residual absorption band at 190–210 nm is associated to the formation of carboxylic acids. In contrast, the addition of barium chloride (BaCl₂) to the irradiated final solution, adjusted with HCl (acidic media), led to the formation of insoluble barium sulfate (BaSO₄). This indicates that the sulfate ions (SO₄²⁻) were formed by the oxidation of the sulfite ions in aerobic condition during the photocatalytic reaction, as was suggested in Section 3.2.

Similar behavior was obtained when the 4-NP solution contained 4 mM of Na₂SO₃ in anaerobic conditions (Fig. 5A). Both absorption bands associated to the SO₃²⁻ ions (at 220 nm) and 4-NP species (at 345 nm), respectively, decreased as time progressed, therefore indicating that both species were eliminated through an oxidation process. Although O₂ concentration is very low (Fig. 3B), the degradation process of both species may be achieved through other mechanisms, for example, by the OH[•] radical formation. In contrast, when 8 mM of Na₂SO₃ was used for the photocatalytic reaction (Fig. 5B), the absorption band of the SO₃²⁻ ions was unaltered with reaction time. The absorption band of the 4-NPhenolate decreased as the time progressed, while a new absorption band appeared at 300 nm, indicating the 4-Aminophenol (4-AP) formation [11]. Additionally, the presence of the absorption band at 230 nm (associated to the aromatic ring of the 4-AP) after the elimination of SO₃²⁻ ions in the final irradiated solution (dash line), confirms that the 4-NP was photoreduced to 4-AP during the UV light irradiation with CdS and in the presence of sulfite ions in anaerobic condition, as previously reported [17]. Similar behavior (degradation process at 4 mM and reduction process at 8 mM of Na₂SO₃) was obtained when N₂ atmosphere (anaerobic condition) was used, since the sulfite concentration was also maintained during all the photocatalytic

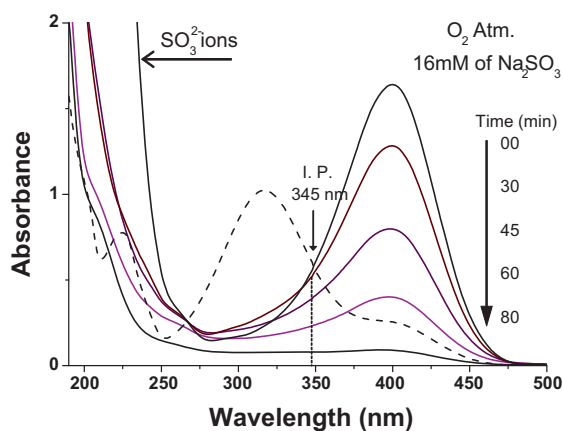


Fig. 4. UV-vis absorbance spectra for the degradation of 4-NP with 16 mM of Na₂SO₃ in aerobic conditions using 0.05 g/L of CdS photocatalyst under UV light irradiation.

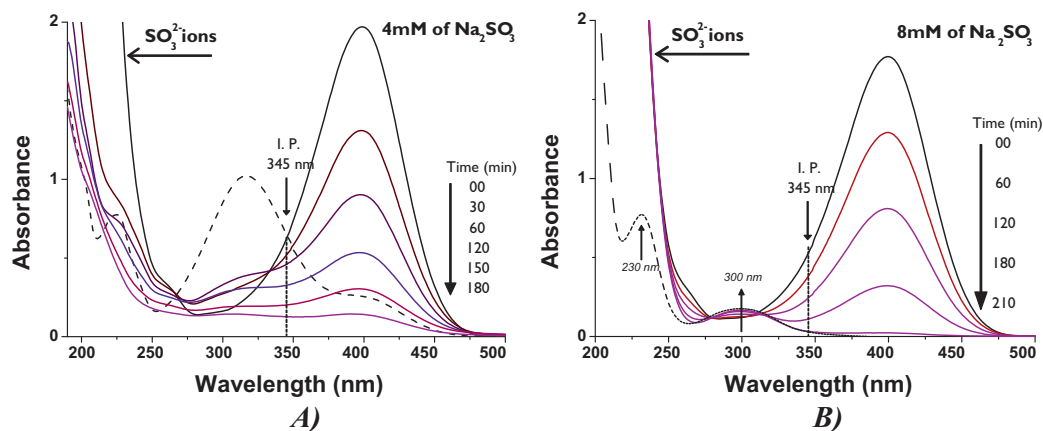


Fig. 5. UV-vis absorbance spectra for 4-NP degradation and 4-NP reduction in the presence of: (A) 4 mM and (B) 8 mM of Na_2SO_3 , respectively, in anaerobic conditions (without O_2 atmosphere) under UV light irradiation.

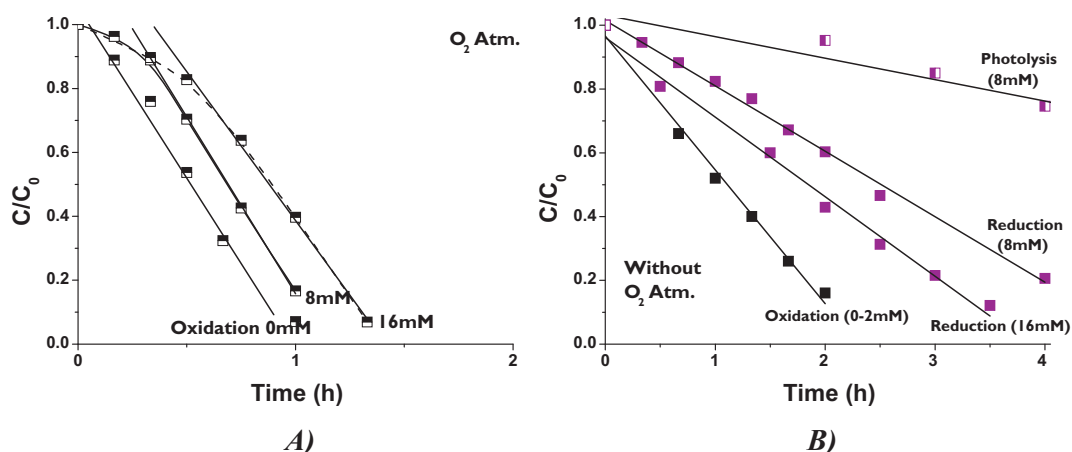


Fig. 6. Kinetic curve for the photocatalytic reaction at different Na_2SO_3 concentrations in: (A) aerobic and (B) anaerobic conditions, under UV light irradiation.

reaction. This result suggests that the oxidation reactions of both species (sulfite and 4-NPhenolate) were inhibited.

3.4. Effect of Na_2SO_3 contents in the 4-NP reaction

The effect of Na_2SO_3 concentration on the 4-NP degradation or reduction kinetics is shown in Fig. 6A and B for the 4-NPhenolate reaction (15 ppm) at different Na_2SO_3 concentrations in either aerobic or anaerobic conditions (without O_2 atm.), under UV light irradiation, respectively. The kinetic curve for either the photo-oxidation or photo-reduction reaction was adjusted to zero order, where the disappearance rate of the reactant is maintained with time. This suggests that the reaction rate is independent of the 4-NPhenolate or 4-NP concentration at different sulfite concentrations. However, the kinetic curve for the 4-NP degradation with 8–16 mM of Na_2SO_3 in aerobic condition (Fig. 6A) was retarded by an induction period. This is due to the oxidation of all sulfite ions during the first ~45 min (Fig. 3B). After the sulfite consumption and the resulting formation of the sulfate (30 min), the degradation process was carried out and the degradation rate was adjusted to zero order once again. Similar kinetic curve adjusted to zero order was obtained for either photooxidation or photoreduction reaction in N_2 atmosphere.

Fig. 7 shows the apparent zero order rate constant for the 4-NP degradation or reduction reaction as a function of sulfite concentration under different atmosphere conditions. When aerobic conditions were used the degradation reaction was predominant

at different ranges of sulfite concentration, with a slight increase of the rate constant value at 8–16 mM sulfite. Conversely, when the photocatalytic reaction was conducted in both anaerobic conditions (without O_2 or with N_2 atmosphere) a different behavior was obtained, which was strongly influenced by the sulfite concentration. At Na_2SO_3 concentrations of less than 4 mM the degradation process was achieved, but when the Na_2SO_3 concentrations was higher than 4 mM, both oxidation and reduction reactions

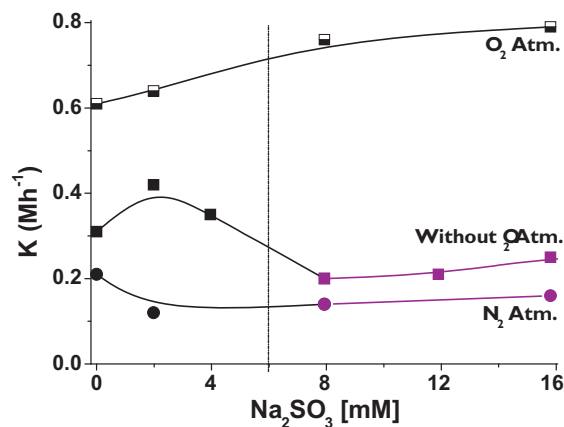


Fig. 7. Profile of the apparent zero order rate constant value as a function of Na_2SO_3 concentration at different atmosphere conditions, under UV light irradiation.

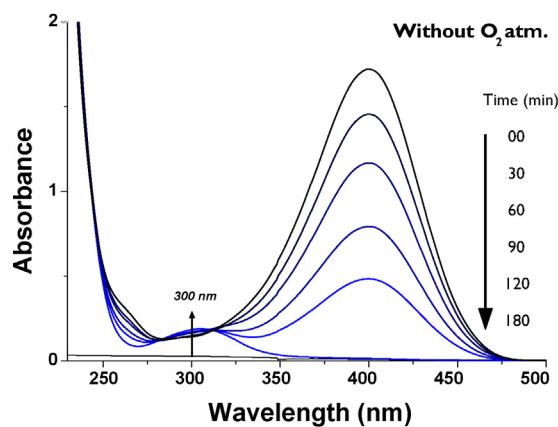


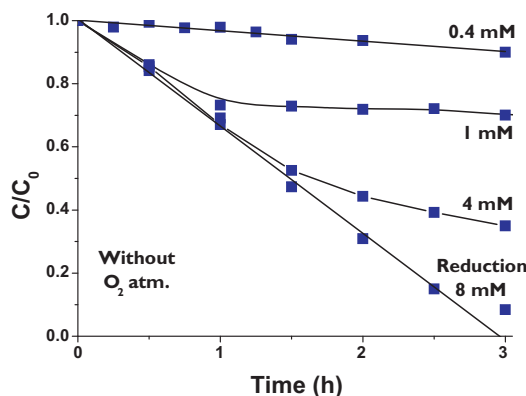
Fig. 8. UV-vis absorbance spectra for 4-NP reduction in presence of Na_2SO_3 at 8 mM in anaerobic conditions, using 0.05 g/L of CdS under blue light irradiation.

compete with each other. The reduction reaction is then favored when the Na_2SO_3 concentration was 8 mM, after which there is a slight increase up to 16 mM.

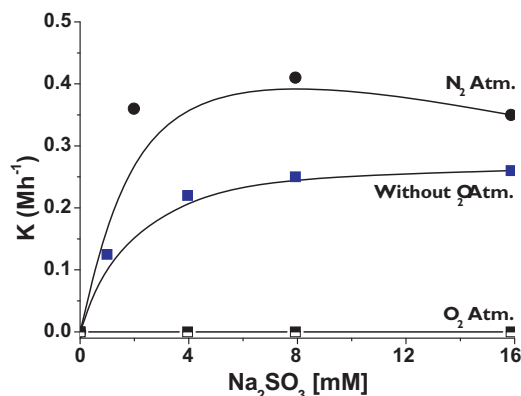
3.5. Reduction of 4-NP under visible light

Considering that the CdS is active under blue light, the photocatalytic 4-NP reduction reaction was carried out under this visible light irradiation. Fig. 8 shows the UV-vis absorbance spectra for the 4-NP reduction reaction in the presence of 8 mM Na_2SO_3 in anaerobic conditions under blue light irradiation. The decreasing of the 4-NP absorption band as the time progressed, together with the appearance of the adsorption band at 300 nm associated to the 4-AP formation indicates that the 4-NP was reduced under blue light irradiation with CdS in the presence of sulfite ions.

Fig. 9A shows the kinetic curve for the 4-NP reduction reaction at different sulfite concentrations. The reduction rate was adjusted to zero order as was obtained under UV light irradiation (Fig. 6B); however, for Na_2SO_3 concentrations between 1 and 4 mM the reduction reaction rate was similar to the 8 mM in the first hour. After that, the 4-NP reduction was not achieved, due to the decreasing of Na_2SO_3 concentrations. This behavior suggests that the conversion of 4-NP to 4-AP is low. Fig. 9B shows the apparent zero order rate constant for the 4-NP reduction as function of Na_2SO_3 concentrations under different atmosphere conditions



A)



B)

Fig. 9. (A) Kinetic curve of the 4-NP reduction and (B) the apparent zero order rate constant for the 4-NP reduction as function of the Na_2SO_3 concentrations in anaerobic conditions under blue light irradiation.

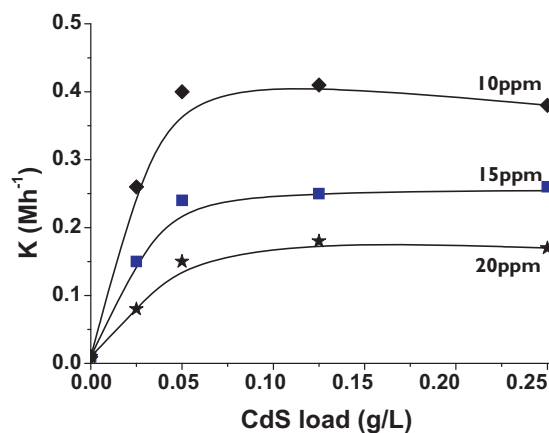


Fig. 10. Profile of the apparent rate constant value for the 4-NP reduction of solutions with different 4-NP concentrations as function of CdS load under blue light irradiation.

and under blue light irradiation. The reduction reaction rates were similar when the Na_2SO_3 concentrations ranged from 4 to 16 mM. The same behavior was obtained when the reduction reaction was carried out in N_2 atmosphere. Conversely, the 4-NP reduction was negligible under O_2 atmosphere (Fig. 9B).

3.6. Effect of CdS load on the 4-NP reduction

Fig. 10 shows the profile of the apparent rate constant for the reduction of 4-NP as function of photocatalyst load at different initial 4-NP concentrations. The apparent zero order rate constant for the 4-NP reduction increases with CdS load at low contents (<0.05 g/L), but when the photocatalyst load exceeds 0.05 g/L, the apparent rate constant value is maintained. This suggests that the reaction follows the Langmuir-Hinshelwood mechanism, where all the photoactive sites are covered by 4-NP molecules. This behavior suggests that the 4-AP desorption could be the controlling step. When the photocatalyst load is higher than 0.25 g/L, the reduction reaction rate begins to decrease probably due to several factors. One of them might be that the particles begin to aggregate themselves, thus reducing the interfacial area between the reaction solution and the photocatalyst, and as consequence reducing the number of photoactive sites on the photocatalyst surface. Furthermore, the lamp luminous fluxes are low and cannot illuminate all the particle surface, then the turbid effect in the

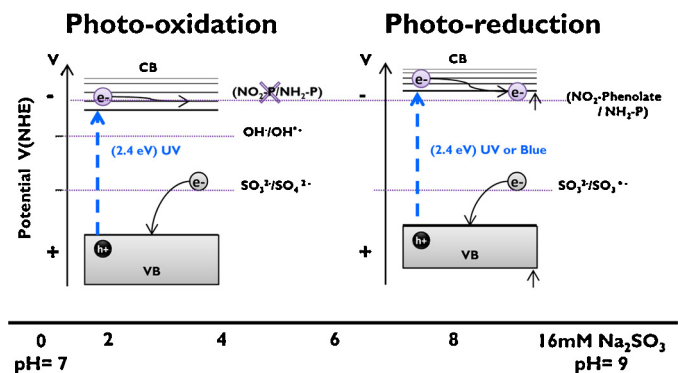


Fig. 11. Potential diagram for the photooxidation of 4-NP or photoreduction of the 4-NP in presence of Na_2SO_3 contents, using CdS as photocatalyst under UV or visible light irradiation.

solution reduces the generation of photoactive sites and as consequence the photocatalytic activity decreases. The photoreduction reaction without photocatalyst was negligible, suggesting that the reaction proceeded via photocatalytic reaction.

In addition, when the initial 4-NP concentration is low (10 ppm) the number of available photoactive sites is high and is possible to achieve a fast rate constant. In contrast, when the 4-NP concentration increases, these available photoactive sites decrease due to the increase of both 4-NP and 4-AP molecules adsorbed on the CdS particle surface. Considering that the lamp luminous fluxes do not varied with time, the numbers of electrons generated remain constant. Therefore, the amount of 4-NP adsorbed onto CdS particles surface is limited by the initial high concentration of 4-AP adsorbed, thus causing an inhibition process and the decrease of the total yield. This effect has been extensively reported for the degradation process using TiO_2 as photocatalysts [23–25].

3.7. Mechanism of the 4-NP oxidation or reduction

According to the results, we propose that the 4-NP or 4-NPphenolate can be eliminated by either oxidation to organic acids or reduction to 4-AP, respectively, by different reaction mechanism, depending on the Na_2SO_3 content, atmosphere conditions and light irradiation (Fig. 11). When the Na_2SO_3 content in the 4-NP solution is higher than 8 mM in anaerobic conditions, the position of the conduction band of CdS ($E_{\text{CB}} = -0.6 \text{ V}$ [27]) may be favorably negative as has been inferred by several authors (-0.8 to -1.0 V at $\text{pH} = 9$) [28,29] and considering that the redox potential for the couples 4-NPphenolate/4-AP is -0.7 V [26], during the photocatalytic reaction under UV or blue light the photogenerated holes (h^+) react with the SO_3^{2-} ions to form sulfite radicals ($\text{SO}_3^{\bullet-}$), while the photogenerated electrons (e^-) are transferred from the conduction band of CdS to the acceptor reactant molecule (4-NPphenolate) [17], favoring the reduction process. In contrast, concentrations of Na_2SO_3 of less than 4 mM allow all the sulfite oxidation to the sulfate formation and as consequence the (E_{CB}) of CdS appears to be unaltered and the electron transfer is not appropriated for the 4-NPphenolate reduction. However, when UV light irradiation is used, the degradation process is detected and it can be done by the presence of hydroxyl radical (OH^{\bullet}), which are generated by the photolysis of water under UV light irradiation [5]. These hydroxyl radicals present an adequate oxidation potential, which are considered as strong oxidant agents capable of oxidizing organic compounds like 4-NP to organic acids [30].

On the other hand, when the photocatalytic reaction is carried out in aerobic conditions under UV light, the high O_2 concentration induces the fast sulfite oxidation to the formation of the sulfate [21]. Such decrease of the sulfite concentration is accompanied with

the generation of OH^{\bullet} radicals which are responsible for the 4-NP degradation. But, when the blue light irradiation is used the sulfite ions are consumed, probably by the photogenerated holes and the CdS photocatalyst is photocorroded. Consequently, the 4-NP degradation is not carried out, since the blue energy is not sufficiently powerful to induce the photolysis of water. Therefore, the oxidation or reduction reaction is achieved in the presence of the appropriate sulfite concentration in anaerobic condition under appropriate UV or visible light irradiation.

4. Conclusions

The degradation of 4-NP was achieved at different sulfite concentrations in aerobic conditions under UV light irradiation. However, the 4-NP degradation or reduction reaction was carried out depending of the Na_2SO_3 concentration in anaerobic conditions. At Na_2SO_3 concentrations of less than 4 mM, the OH^{\bullet} radical formation induce the oxidation of the both sulfite and 4-NP. Furthermore, at Na_2SO_3 concentrations higher than 8 mM, the 4-NP reduction is favored via an electron transfer process from the photocatalyst surface to the 4-NPphenolate species. Under blue light irradiation only the reduction reaction was obtained in anaerobic conditions. The 4-NP degradation and reduction reactions follow a kinetic of zero order and they can be used for the evaluation of active photocatalysts under UV or visible light.

Acknowledgments

Agileo Hernandez-Gordillo would like to acknowledge CONACyT-México for an scholarships and the 34856 grant supporting this research. The study was supported by the CONACyT-SEP CB-157156 grant and CONACyT FOINS Artificial Photosynthesis.

References

- [1] W. Zhan, F. Tan, W. Wang, X. Qiu, J. Chen, *Journal of Hazardous Materials* 217/218 (2012) 36–42.
- [2] C. Datta, R. Naidu, M.K.N. Yenkie, *Journal of Scientific and Industrial Research* 63 (2004) 518–521.
- [3] V. Uberoi, S.K. Bhattacharya, *Water Environment Research* 69 (1997) 146–156.
- [4] Y. Shaoqing, H. Jun, W. Jianlong, *Radiation Physics and Chemistry* 79 (2010) 1039–1046.
- [5] S. Zhao, H. Ma, M. Wang, C. Cao, J. Xiong, Y. Xuc, S. Yao, *Photochemical and Photobiological Sciences* 9 (2010) 710–715.
- [6] D. Chen, A.K. Ray, *Water Research* 32 (1998) 3223–3234.
- [7] C.-H. Chiou, C.-Y. Wu, R.-S. Juang, *Separation and Purification Technology* 62 (2008) 559–564.
- [8] V. Maurino, C. Minero, E. Pelizzetti, P. Piccinini, N. Serpone, H. Hidaka, *Journal of Photochemistry and Photobiology A: Chemistry* 109 (1997) 171–176.
- [9] W.-Y. Ahn, S.A. Sheeley, T. Rajh, D.M. Crokek, *Applied Catalysis B: Environmental* 74 (2007) 103–110.
- [10] H. Koga, T. Kitaoka, *Chemical Engineering Journal* 168 (2011) 420–425.
- [11] K. Kuroda, T. Ishida, M. Haruta, *Journal of Molecular Catalysis A: Chemical* 298 (2009) 7–11.
- [12] P. Liu, M. Zhao, *Applied Surface Science* 255 (2009) 3989–3993.
- [13] B. Naik, S. Hazra, V.S. Prasad, N.N. Ghosh, *Catalysis Communications* 12 (2011) 1104–1108.
- [14] J. Zhang, G. Chen, M. Chaker, F. Rosei, D. Ma, *Applied Catalysis B: Environmental* 132/133 (2013) 107–115.
- [15] G. Falcone, O. Giuffrè, S. Sammartano, *Journal of Molecular Liquids* 159 (2011) 146–151.
- [16] S. Gazi, R. Ananthakrishnan, *Applied Catalysis B: Environmental* 105 (2011) 317–325.
- [17] A. Hernández-Gordillo, A.G. Romero, F. Tzompanzi, R. Gomez, *Journal of Photochemistry and Photobiology A: Chemistry* 257 (2013) 44–49.
- [18] F. Li, W. Bi, T. Kong, C. Wang, Z. Li, X. Huang, *Journal of Alloys Compound* 479 (2009) 707–710.
- [19] G. Pandey, S. Dixit, *The Journal of Physical Chemistry C* 115 (2011) 17633–17642.
- [20] Y. Li, Y. Hu, S. Peng, G. Lu, S. Li, *The Journal of Physical Chemistry C* 113 (2009) 9352–9358.
- [21] I. Fridovich, P. Handler, *The Journal of Biological Chemistry* 235 (6) (1960) 1835–1838.
- [22] N. Oshino, B. Chance, *Archives of Biochemistry and Biophysics* 170 (1975) 514–528.

- [23] J. Lee, A. Adesina, *Journal of Chemical Technology and Biotechnology* 76 (2001) 803–810.
- [24] T. Zhang, L. You, Y. Zhang, *Dyes and Pigments* 28 (2006) 95–100.
- [25] D. Chen, A.K. Ray, *Water Research* 32 (11) (1998) 3223–3234.
- [26] S.K. Ghosh, M. Mandal, S. Kundu, S. Nath, T. Pal, *Applied Catalysis A: General* 268 (2004) 61–66.
- [27] N. Bühler, K. Meier, J.-F. Reber, *The Journal of Physical Chemistry* 88 (1984) 3261–3268.
- [28] O.L. Stroyuk, O.Y. Rayevska, A.V. Kozytskiy, S.Y. Kuchmiy, *Journal of Photochemistry and Photobiology A: Chemistry* 210 (2010) 209–214.
- [29] L. Stroyuk, A.V. Korzhak, A.E. Raevskaya, S. Ya Kuchmii, *Theoretical and Experimental Chemistry* 40 (2004) 1–6.
- [30] P. Neta, R.E. Huie, *Environmental Health Perspectives* 64 (1985) 209–217.